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14. ABSTRACT

A model-based simulation (MBS) capability for tailoring the fabrication processes and the properties of wide band gap semiconductors thin films (TF) with engineered nanoscale porosity has been achieved in two ways:

1. By using molecular dynamics simulations (MDS) to relate a given set of deposition parameters to the resulting microstructure.

2. By developing a novel bending theory for a continuum body with microstructure.

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MODEL-BASED SIMULATIONS TO ENGINEER NANOPOROUS THIN FILMS

AFOSR GRANT F49620-02-1-0106

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Relevancy

Objectives

This project will create a model-based simulation (MBS) capability for tailoring the fabrication processes and the properties of wide band gap semiconductors thin films (TF) with engineered nanoscale porosity via the:

1. computational prediction of the morphology of a TF as it derives from a given set of deposition parameters;

2. theoretical determination of the deposition conditions leading to the creation of a given target nanostructure;

3. computational prediction of mechanical properties such as the porosity distribution throughout the film, assessment of its mechanical stability along with the spatial distributions of the intrinsic stresses, interfacial fracture toughness, and (heterogeneous) elastic moduli as well as their symmetry properties;

4. development of advanced bending theory of TFs and computational measure of the constitutive parameters required for these theories. This will contribute to future developments in which *in situ* measurements of the spatial distribution of TF curvature are used for the real-time estimation of the intrinsic stresses in nanoporous TFs.

Approach.

The project's objectives will be achieved in two ways:

1. By using molecular dynamics simulations (MDS) to relate a given set of deposition parameters to the resulting microstructure. These simulations, although generalizable to every material system for which interaction potentials are known, will focus on MgF_2, SiC, and GaN as specific material systems.

2. By developing a novel bending theory for a continuum body with microstructure. Specifically, we will formulate a bending theory for columnar and porous TFs so as to explicitly account for the presence of a specific microstructure in the estimation of stress levels and mechanical stability.

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Background on the prediction of mechanical properties of TFs

Research over the past 15 years [10, 15, 18, 20, 21, 24, 29] has identified various methods to understand the mechanical behavior of compliant substrates. In addition, methods to assess the substrate/film interface stability have also been considered [14, 29]. These methods include molecular dynamics [12] and continuum mechanics [5, 10, 11, 14, 15, 18, 20, 21, 24, 29]. Other studies on the mechanisms of deformation at the nanoscale have included a combination of molecular simulations and continuum analyses [1].

The reasons for determining the elastic moduli (EM) are many. First of all, the EM are the fundamental property that one needs to correlate the TF macroscopic deformation to the internal stress state. Secondly, EM are correlated with properties such as hardness and wave speed velocities, that is, properties which can be measured via current experimental techniques. In addition, knowledge residual stresses (RS) and EM at the very fine scale allows one to determine these same properties at courser scales by simply computing their spatial averages. This is highly desirable because it allows one to enhance current experimental techniques which estimate TF stresses via optical measurements of the film/substrate system curvature.

The theoretical and experimental estimation of TF intrinsic stresses has been studied by several authors (see [2, 3, 6, 8, 13, 16, 17, 22, 23, 25, 27, 28, 30]). The majority of these studies are devoted to high density and often crystalline TFs. For these materials, the relations between experimentally measured quantities (such as TF curvature) and the intrinsic stresses, such as Stoney's relation [26] and variants thereof (*cf.* [7] and [19]), have often been established via continuum analyses where the film is viewed as a homogeneous and almost always isotropic material. More recently, approaches that take into account the through-the-thickness variation of RS and EM in compositionally graded thin films have been considered (see, *e.g.*, [3, 4, 9]). Unfortunately, these methods do not apply in cases where there is a high degree of inhomogeneity and in which the dominant morphological feature is the architecture of the film's columns. For these reasons, a new approach is needed in which the spatial distribution of porosity and the columnar morphology is clearly reflected in the curvature/stress relations.

Background Information and Partnerships

Achieving the project's objectives will provide the scientific and engineering communities with the ability to *engineer* nanoporous TFs structures with specified porosity, morphology, and mechanical properties. In addition, we will develop, and correlate with experiments, the ability to connect spatial curvature measurements with intrinsic stresses in TFs. The aspect of using discrete information at the nanoscale to create a bridge to analysis at continuum scales is of great import for the mechanical analysis of nano-structures, micro-structures, and micro-electro-mechanical systems (MEMS).

A partnership with Prof. Russell Messier of The Pennsylvania State University exists for the purpose of correlating experimentally determined TF morphology as a function of deposition parameters with the theoretically determined counterparts. The present AFOSR-funded work is an outgrowth of an NSF grant (CMS-9733653) obtained by F. Costanzo on the mechanical properties of sculptured TFs.

Innovation in Science

To date, we have:

- Researched and assembled a library of potentials for the materials systems of interest. Each of the materials systems involves either a pairwise or many-body potential—some systems include both types.
- The library of potentials has been implemented in a parallel MD code for open systems that simulates the deposition of TFs.
- Software has been developed that uses the appropriate potential for each MD-deposited system and calculates stresses and moduli within the film.
- We have expanded continuum homogenization notions of effective properties to apply to systems undergoing large deformations and applicable to a full dynamic context.
- We formulated a new Lagrangian-based MD scheme which includes the automatic computation of the mechanical properties of a thermo-elastic system in a regime of large deformation.
- We have formulated a novel bending theory, which uses the concept of *director* to specifically account for the columnar microstructure of the films of interest. Furthermore, the theory we have developed has been derived as a continuum counterpart of a discrete model, which allows one to provide a simple physical interpretation of the solutions predicted by the continuum theory.
- The developed director-based TF bending theory has been used in a series of "proof-of-concept" calculations to show that the deformation behavior of a columnar and/or porous TF can depart substantially from that predicted by current techniques for the estimation of the stress in TF.

The main scientific results obtained so far are:

1. The derivation of a procedure for determining continuum properties from discrete information (i.e., MD). This procedure is consistent with homogenization theory and shows that the concept of virial stress, namely the typical stress measure used in MD calculations of mechanical properties in solids, is a meaningful stress measure only under a very restrictive set of assumptions. By contrast, we have proposed a stress measure that is is much more general and that recovers that provided by the virial stress under the restrictive assumption that make the concept of virial stress meaningful.
2. Our preliminary calculations, based on the director-based bending theory we have developed, show that a stress state assessment based on the standard Euler-Bernoulli bending theory* can yield to gross misinterpretation of the actual stress/strain.

The research conducted so far has resulted in the following conference presentation and refereed publications acknowledging AFOSR sponsorship:

*The Euler-Bernoulli begin theory, i.e., the elementary bending theory of Strength of Materials, is the *de facto* state of the art in stress measurement for TFs based on optical curvature measurement of the TF substrate.

1. Costanzo, F., Gray, G. L., and Andia, P. C., "On the Notion of Average Mechanical Properties in MD Simulation via Homogenization," *Modelling and Simulation in Materials Science and Engineering*, **12**, pp. S333–S345,2004.

2. Costanzo, F., Gray, G. L., Andia, P. C., "On the Definitions of Effective Stress and Deformation Gradient for Use in MD: Hill's Macro-homogeneity and the Virial Theorem," *International Journal of Non-Linear Mechanics*, submitted, 2004.

3. Andia, P. C., Costanzo, F., and Gray, G. L., "A Continuum Homogenization Model for Heterogeneous Media Using a Lagrangian-Based Approach," *International Journal of Solids and Structures*, submitted, 2004.

4. Gray, G. L., Costanzo, F., Andia, P. C., and Yurick, T., "Determination of the Mechanical Properties of Amorphous Columnar Thin Films from MD Simulations," *Proceedings of the 7th US National Congress on Computational Mechanics*, Albuquerque (NM), July 28–30, 2003, CD-ROM ISBN: 0-9743254-0-6.

5. Randow, C. L., Gray, G. L., and Costanzo F., "A Polar Continuum Model of a Columnar Thin Film," *Proceedings of Eccomas 2004: European Congress on Computational Methods in Applied Sciences and Engineering*, Jyväskylä, Finland, July 24–28, 2004.

Innovation in Design

Nanoporous TFs made from wide band gap semiconductors, which include SiC and the group III nitrides, are being explored by a number of researchers for a wide range of applications. For example, porous SiC is of interest for chemical sensing and much work has been done on porous Si sensors, with which a wide variety of gases have been sensed. In addition, researchers are currently studying porous SiC and GaN onto which transition metals, transition metal oxides, and metallic sulfides have been deposited for use as catalysts. Nanoporous sculptured TFs (NSTFs), in particular, are of interest for short wavelength optical devices. NSTFs possess unique porous nanostructures that can be realized by rotating the substrate during film growth. For example, these nanostructures, possessing right- or left-handedness, provide a way of distinguishing right-circular and left-circular polarizations of light. We are developing a model-based simulation (MBS) capability to engineer the morphology and mechanical properties of nanoporous TFs.

In constructing the proposed MBS capability, we intend to establish a methodology to bridge length scales ranging a few nanometers to microns. By incorporating information gathered by atomistic simulations into nonlinear continuum models, the approach can be generalized to address a number of issues that are important in MEMS. These issues include measures of surface hardness, interfacial friction, interfacial fracture toughness, and resistance to fatigue.

References

[1] F. F. Abraham, D. Brodbeck, W. E. Rudge, J. Q. Broughton, D. Schneider, B. Land, D. Lifka, J. Gerner, M. Rosenkrantz, J. Skovira, and H. Gao, Ab Initio *dynamics of rapid fracture*, Modelling and Simulation in Materials Science and Engineering, 6 (1998), pp. 639–670.

[2] P. S. ALEXOPOULOS AND T. C. O'SULLIVAN, *Mechanical properties of thin films*, Annual Review of Materials Science, 20 (1990), pp. 391–420.

[3] S. P. BAKER AND W. D. NIX, *Intrinsic stresses in compositionally modulated Au-Ni thin films and the supermodulus effect*, Journal of Materials Research, 9 (1994), pp. 3145–3152.

[4] ——, *Mechanical properties of compositionally modulated au-ni thin films: Nanoindentation and microcantilever deflection experiments*, Journal of Materials Research, 9 (1994), pp. 3131–3144.

[5] K. BHATTACHARYA AND R. D. JAMES, *A theory of thin films of martensitic materials with applications to microactuators*, Journal of the Mechanics and Physics of Solids, 47 (1999), pp. 531–576.

[6] B. M. CLEMENS AND J. A. BAIN, *Stress determination in textured thin films using x-ray diffraction*, MRS Bulletin, 17 (1992), pp. 46–51.

[7] D. E. FAHNLINE, C. B. MASTERS, AND N. J. SALAMON, *Thin film stress from nonspherical substrate bending measurements*, Journal of Vacuum Science and Technology A, 9 (1991), pp. 2483–2487.

[8] L. B. FREUND, *The stress distribution and curvature of a general compositionally graded semiconductor layer*, Journal of Crystal Growth, 132 (1993), pp. 341–344.

[9] ——, *Some elementary connections between curvature and mismatch strain in compositionally graded thin films*, Journal of the Mechanics and Physics of Solids, 44 (1996), pp. 723–736.

[10] L. B. FREUND AND W. D. NIX, *A critical thickness condition for a strained compliant substrate/epitaxial film system*, Applied Physics Letters, 69 (1996), pp. 173–175.

[11] G. FRIESECKE AND R. D. JAMES, *A scheme for the passage from atomic to continuum theory for thin films, nanotubes and nanorods*, Journal of the Mechanics and Physics of Solids, 48 (2000), pp. 1519–1540.

[12] M. R. GUNGOR, D. MAROUDAS, AND S. ZHOU, *Molecular-dynamics study of the mechanism and kinetics of void growth in ductile metallic thin films*, Applied Physics Letters, 77 (2000), pp. 343–345.

[13] S. HONG, T. P. WEIHS, J. C. BRAVMAN, AND W. D. NIX, *Measuring stiffnesses and residual stresses of silicon nitride thin films*, Journal of Electronic Materials, 19 (1990), pp. 903–909.

[14] J. HU AND P. H. LEO, *Defect structures at thin film-substrate interfaces*, Journal of the Mechanics and Physics of Solids, 45 (1997), pp. 637–665.

[15] F. Y. HUANG, *Effect of strain transfer on critical thicknesses for epitaxial layers grown on compliant substrate*, Applied Physics Letters, 76 (2000), pp. 3046–3048.

[16] G. L. HUFFMAN, D. E. FAHNLINE, R. MESSIER, AND L. J. PILIONE, *Stress dependence of reactively sputtered aluminum nitride thin films on sputtering parameters*, Journal of Vacuum Science and Technology A, 7 (1989), pp. 2252–2255.

[17] H. T. JOHNSON AND L. B. FREUND, *Mechanics of coherent and dislocated island morphologies in strained epitaxial material systems*, Journal of Applied Physics, 81 (1997), pp. 6081–6090.

[18] D. MAROUDAS, L. A. ZEPEDA-RUIZ, AND W. H. WEINBERG, *Kinetics of strain relaxation through misfit dislocation formation in the growth of epitaxial films on compliant substrates*, Applied Physics Letters, 73 (1998), pp. 753–755.

[19] C. B. MASTERS, *A Geometrically Nonlinear Stress-Deflection Relation for Thin Film/Substrate Systems*, Ph.D., The Pennsylvania State University, 1992.

[20] J. W. MATTHEWS AND A. E. BLAKESLEE, *Defects in epitaxial multilayers I. misfit disclocations.*, Journal of Crystal Growth, 27 (1974), pp. 118–125.

[21] ——, *Defects in epitaxial multilayers II. dislocation pile-ups, threading dislocations, slip lines and cracks.*, Journal of Crystal Growth, 29 (1975), pp. 272–280.

[22] E. D. NICHOLSON AND J. E. FIELD, *The mechanical and thermal properties of thin films*, Journal of Hard Materials, 5 (1994), pp. 89–132.

[23] W. D. NIX, *Mechanical properties of thin films*, Metallurgical Transactions A, 20A (1989), pp. 2217–2245.

[24] R. PEOPLE AND J. C. BEAN, *Calculation of critical layer thickness versus lattice mismatch for* Ge_xSi_{1-x}/Si *strained-layer heterostructures*, Applied Physics Letters, 47 (1985), pp. 322–324.

[25] J.-Å. SCHWEITZ, *Mechanical characterization of thin films by micromechanical techniques*, MRS Bulletin, 17 (1992), pp. 34–45.

[26] G. G. STONEY, *The tension of metallic films deposited by electrolysis*, Proceedings of the Royal Society of London, A 82 (1909), pp. 172–175.

[27] C. V. THOMPSON AND R. CAREL, *Stress and grain growth in thin films*, Journal of the Mechanics and Physics of Solids, 44 (1996), pp. 657–673.

[28] R. VENKATRAMAN, J. C. BRAVMAN, W. D. NIX, P. W. DAVIES, P. A. FLINN, AND D. B. FRASER, *Mechanical properties and microstructural characterization of al-0.5%cu thin films*, Journal of Electronic Materials, 19 (1990), pp. 1231–1237.

[29] L. A. ZEPEDA-RUIZ, D. MAROUDAS, AND W. H. WEINBERG, *Theoretical study of the energetics, strain fileds, and semicoherent interface structures in layer-by-layer semiconductor heteroepitaxy*, Journal of Applied Physics, 85 (1999), pp. 3677–3695.

[30] V. ZIEBART, O. PAUL, U. MÜNCH, J. SCHWIZER, AND H. BALTES, *Mechanical properties of thin films from the load deflection of long clamped plates*, Journal of Microelectromechanical Systems, 7 (1998), pp. 320–328.